

Communication

Magnetic Catalyzed Fenton Oxidation by CuO/ns-Fe₃O₄ for Modification of Humic Acids

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Abstract

Humic acids (HAs) are widely used as adsorbents or carriers, yet they still lack oxygenic functional groups under certain conditions. Modification via catalytic oxidation under mild conditions is an ideal method to increase the oxygenic functional groups in HAs—if simple catalyst separation could be realized. Here, we report the use of CuO nanoparticles supported by Fe₃O₄ magnetic nanospheres as magnetic catalytic systems (MCSs) that could catalyze HA modification via Fenton oxidation. These MCSs can be easily magnetically separated from the products. The content of carboxyl groups increased from 2.45% to 10.47% after reaction, while the yield of modified HAs remained approximately 100%. These results indicate that oxidation with MCSs could be a potential method for HA modification.

Keywords: MCSs; Fenton oxidation; humic acids modification; oxygenic functional groups

1. Introduction

Humic acids (HAs) are widely used in agriculture, pharmaceuticals and fine chemicals [1,2] as a kind of natural organic polymer which is decomposed and synthesized from animal and plant residues under the action of microorganisms and geochemistry. Certain oxygenic functional groups in HAs, such as carboxyl and quinonyl groups [3–5], provide appropriate sorption capacity to adsorb fertilizers or active drug ingredients. Lignite (low rank coal) is an important material for HA extraction [2,6]. However, HAs from lignite generally lack oxygenic functional groups, which limits their use as adsorbing materials or carriers. Researchers have reported a method to increase oxygenic functional groups by oxidizing HAs during the extraction from lignite [7,8]. However, in most cases, the yields of HAs are decreased remarkably to reach the adsorbent requirements. Another method to increase the oxygenic functional groups in HAs is modification by catalytic oxidation under mild conditions. The ideal catalytic oxidation modification method for HAs should have a high yield and remarkably increase oxygenic functional groups. However, there is a clear disadvantage of catalytic oxidation modification: the separation of the catalyst and HAs after the reaction.

HAs should remain solid or colloidal in certain situations, especially when used as sustained-release carriers. The feasibility of modification via catalytic oxidation depends on the separation of the catalyst and HAs after the reaction. Among the extensive and diverse collection of heterogeneous catalytic systems, magnetic catalytic systems (MCSs) have attracted increasing attention from scientists due to their substantial benefits, particularly their facile separation during the purification of products [9–14]. Considering the widespread application of Cu-based catalysts in Fenton oxidation systems [15–17] and



Academic Editor: Enric Brillas

Received: 4 November 2025

Revised: 24 November 2025

Accepted: 28 November 2025

Published: 18 December 2025

Citation: Li, T.; Zheng, X.; Hu, X.; Hu, G. Magnetic Catalyzed Fenton Oxidation by CuO/ns-Fe₃O₄ for Modification of Humic Acids. *Catalysts* **2025**, *15*, 1175. <https://doi.org/10.3390/catal15121175>

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the highly developed synthesis methods for Fe_3O_4 -based magnetic materials [18–24], in this work, CuO nanoparticles supported by Fe_3O_4 magnetic nanospheres are designed and prepared as MCSs for the catalytic oxidation of HAs under mild conditions with H_2O_2 as the oxidant. The results show that CuO/ Fe_3O_4 MCSs can effectively increase the content of oxygenic functional groups in HAs, especially carboxyl contents, through Fenton oxidation treatments.

2. Structure and Morphology Analysis

Fe_3O_4 magnetic nanospheres (ns- Fe_3O_4) were prepared according to the literature [24–29] with 0.136 mol/L of templating agents (cetyltrimethylammonium bromide, CTAB) and a series of different weight percentages of CuO supported on ns- Fe_3O_4 MCSs, which were prepared via an impregnation method. These nanospheres were denoted 0.2CuO/ns- Fe_3O_4 for a 0.2% weight fraction and 1CuO/ns- Fe_3O_4 for a 1% weight fraction. Cobalt oxide supported on ns- Fe_3O_4 was also prepared because cobalt oxides are common Fenton oxidation catalysts. This catalyst was denoted 0.2CoO_x/ns- Fe_3O_4 for a 0.2% weight fraction of Co. For all preparation details, see Section 4. Fe_2O_3 and $\alpha\text{-FeOOH}$ were also prepared using methods reported in the literature [30,31] for an exploration of their magnetic and dispersive properties.

Although Fe_2O_3 showed good dispersibility, as shown in Figure 1(b1), its magnetic performance was not significant, and there was no significant magnetization aggregation phenomenon under the action of a magnetic field (Figure 1(b2)). This means that despite its potential catalytic activity, Fe_2O_3 did not meet our expectations for easy magnetic separation and catalyst recovery due to its lack of sufficient magnetism, limiting its application in certain catalytic reactions. $\alpha\text{-FeOOH}$ exhibited better magnetic properties, as shown in Figure 1(c2), but it tended to show some degree of agglomeration before being subjected to magnetic attraction (Figure 1(c1)). This agglomeration behavior could lead to an uneven distribution of the catalyst in actual catalytic reactions, affecting the reaction efficiency and product selectivity. Comparing the magnetic properties and considering yield factors, ns- Fe_3O_4 was chosen as the main catalyst component because it exhibited significant magnetic properties (Figure 1(a2)). It also maintained good dispersibility when no external magnetic field was applied, which can be visually observed in Figure 1(a1). Furthermore, the concentration of the template agent CTAB was also adjusted to modify the size of the nano Fe_3O_4 microspheres while using VSM to determine the optimal preparation conditions for Fe_3O_4 microspheres as supports with suitable magnetic properties. Here, four different concentrations of CTAB were investigated: namely, 0, 0.070, 0.136, and 0.200 mol/L; the optimal concentration was found to be 0.136 mol/L. Therefore, all ns- Fe_3O_4 samples used in this work, unless otherwise noted with a template agent concentration, were prepared under 0.136 mol/L CTAB.



Figure 1. Catalyst morphology and changes caused by magnetic adsorption of ns- Fe_3O_4 (a1,a2), Fe_2O_3 catalytic material (b1,b2), and $\alpha\text{-FeOOH}$ catalytic material (c1,c2).

2.1. High-Resolution Transmission Electron Microscopy (HRTEM) and Energy-Dispersive X-Ray Spectroscopy (EDS) Mapping

TEM analysis of the pristine Fe_3O_4 and $\text{CuO}/\text{Fe}_3\text{O}_4$ nanospheres showed that the pristine Fe_3O_4 nanoparticles (Figure 2a,b) have a spherical shape with a size of around 80–220 nm and typical diameter of 160 nm (Figure 2c). After impregnation to support CuO , as shown in Figure 2d, the particles maintained their original spherical shape and size, and there was an additional layer of light black substance around the dark black Fe_3O_4 nanospheres. According to EDS mapping analysis (Figure 2f), this is due to CuO particles being uniformly loaded on Fe_3O_4 , resulting in the uneven particle color state observed in TEM spectra. In HRTEM images (Figure 2e), all observed nanoparticles exhibit a lattice spacing of approximately 0.48 nm, which matches the interplanar spacing obtained from XRD. This observation indicates that nanoparticle aggregation occurs in an ordered manner along their crystal plane growth direction. TEM was also used to analyze Fe_3O_4 magnetic nanospheres prepared under different CTAB concentrations (Supplementary Information, Figure S1).

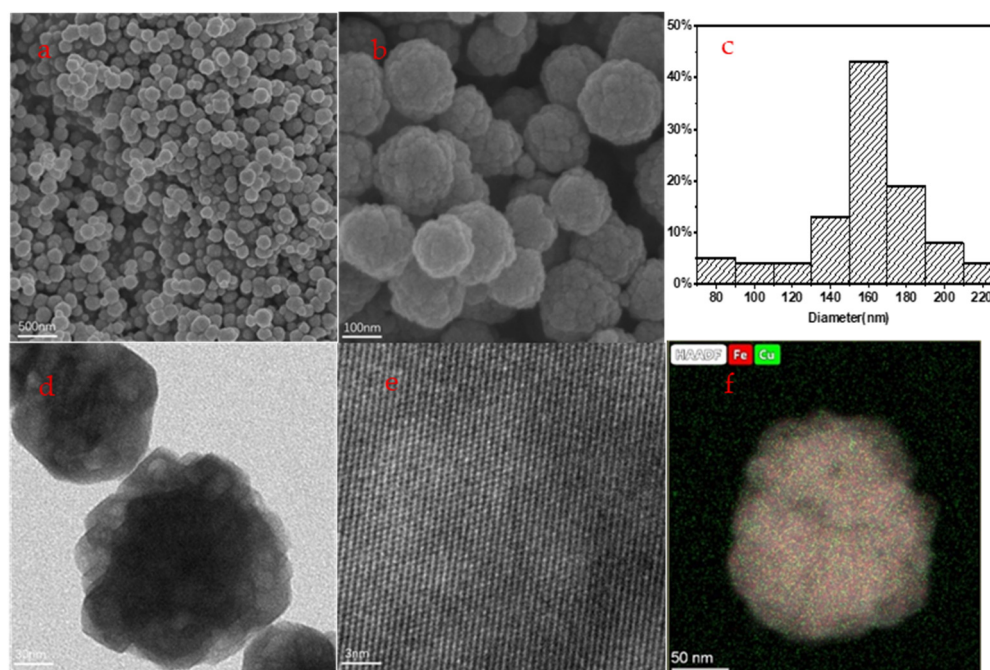


Figure 2. TEM images of pristine Fe_3O_4 (a,b) and $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$ (d); statistical graph of the nanosphere size of pristine Fe_3O_4 (c); HRTEM image of $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$ (e); EDS mapping image of $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$ (f), where red highlights represent Fe and green highlights represent Cu.

2.2. X-Ray Diffraction (XRD)

In XRD patterns of $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$ (Figure S2), six characteristic Fe_3O_4 peaks ($2\theta = 30.2^\circ, 35.5^\circ, 43.1^\circ, 53.4^\circ, 57.0^\circ$, and 62.6°) were observed. These peaks are consistent with the database in the JCPdS file (PCPdFWIN v.2.02) and the literature [21,22,24,28,29,32,33]. These results confirm that Fe_3O_4 nanospheres are composed of smaller secondary nanoparticles. Based on the XRD data, the grain size of $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$ was calculated to be 27.2 nm using the Scherrer formula. This is inconsistent with the Fe_3O_4 grain size of 160 nm estimated from TEM images in the previous section (Figure 2c). Inconsistent sizes between TEM and XRD have also been reported for similar materials [24,34]. It is speculated that this discrepancy may be due to the substructures of $\text{ns-Fe}_3\text{O}_4$, which are formed by the aggregation of smaller nanospheres [34]. The size of $\text{ns-Fe}_3\text{O}_4$ as calculated based on XRD will mainly be affected by the size of the smaller secondary Fe_3O_4 particles and slightly influenced by the packing density of these particles. However, the size of $\text{ns-Fe}_3\text{O}_4$ as

calculated based on TEM will reflect the overall size after aggregation of the secondary Fe_3O_4 particles.

2.3. X-Ray Photoelectron Spectrometry (XPS Spectra)

The elemental distribution and respective valence states of $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$ were verified by X-ray photoelectron spectroscopy (Figure S3). The analysis was conducted according to literature reports [35]. Distinct characteristic peaks of Fe, Cu, and O appeared in the overall spectrum of $\text{Fe}_3\text{O}_4\text{-CuO}$, as shown in Figure S3a. The corrected XPS peaks were identified as Fe2p at 710.0 eV, O1s at 529.5 eV, and Cu2p at 937.08 eV. To confirm the presence of Fe_3O_4 , the Fe2p orbitals were further split, as shown in Figure S3b. The peaks at 710.49 eV and 723.78 eV correspond to the binding energies of $\text{Fe}^{2+}2p_{3/2}$ and $2p_{1/2}$ orbitals, respectively, while the peaks at 713.42 eV and 726.78 eV correspond to those of $\text{Fe}^{3+}2p_{3/2}$ and $2p_{1/2}$ orbitals, respectively. The splitting at 713 eV confirms the metallic state of Fe, and the peaks at 712.23 eV and 731.34 eV are satellite peaks. This demonstrates that the chemical composition of Fe_3O_4 was preserved upon loading CuO. As shown in Figure S3c, the peaks at 937.50 eV and 942.0 eV belong to the shake-up peaks of CuO in the divalent state, confirming the successful loading of CuO onto the material. The peaks in the O1s orbitals at 529.82 eV, 531.23 eV, and 532.04 eV in Figure S3d were assigned to the binding energies of Fe-O-Fe, Fe-O, and Cu-O, respectively. Based on the above XPS analysis, it is evident that CuO supported on Fe_3O_4 magnetic nanomaterials was successfully synthesized.

2.4. Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES)

The results of ICP-OES analysis show that the Cu loading rate is identical to that noted for $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$, $1\text{CuO}/\text{ns-Fe}_3\text{O}_4$, and $0.2\text{CoO}_x/\text{ns-Fe}_3\text{O}_4$ (see details in Table S1, entries 1–3).

2.5. Vibrating Sample Magnetometry (VSM)

VSM is widely used to describe the magnetic properties of materials [18,34]. As shown in Figure S4, the saturation magnetization (M_s) of $0.2\text{CuO}/\text{ns-Fe}_3\text{O}_4$, measured by VSM, is 79.74 emu/g, indicating significant magnetic properties. Other samples of magnetic Fe_3O_4 nanospheres prepared under different CTAB concentrations exhibited superparamagnetic characteristics. In samples without CTAB, the saturation magnetization (M_s) was only 68.26 emu/g. The introduction of CTAB significantly increased the M_s of $0.2\text{CuO}/\text{Fe}_3\text{O}_4$ microspheres, particularly when the CTAB concentration increased in the range of 0.070 to 0.136 mol/L. Although the size of the Fe_3O_4 microspheres increased negligibly, the packing density of the Fe_3O_4 secondary particles increased significantly (Figure S1). This suggests that the gradual increase in sample saturation magnetization was mainly driven by the particle overall size effect. However, when the CTAB concentration reached 0.2 mol/L, a slight decrease in M_s was observed; the reasons for this have not yet been thoroughly investigated in this work. The optimized CTAB concentration was thus obtained.

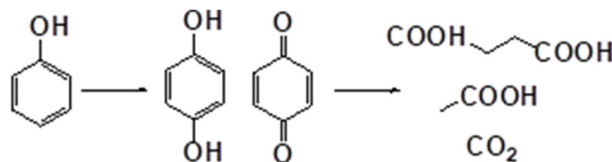
3. Fenton Oxidation

Considering the complexity of the structure of HAs and the imprecision of quantitative descriptions of oxygenic functional group contents, phenol was chosen as the model compound substrate to compare the performances of different MCSs.

3.1. Performance Comparison of Different MCSs for Phenol Oxidation

Phenolic hydroxyl groups are widely present in HAs, and they are generally regarded as weaker acids compared to the carboxyl group, which is another common group found in HAs [7]. The oxidation of carboxyl to CO_2 reduces the complexation ability of HAs, and

there are strict reaction conditions for SP³ C–H bond oxidation; therefore, HA modifications are mainly related to the oxidation of phenolic hydroxyl [36]. The mild reaction conditions of phenolic hydroxyl increase new complexing groups while avoiding carboxyl oxidation (Scheme 1). Herein, phenol oxidation was used as a probe reaction to investigate the activities of the studied catalysts.



Scheme 1. Oxidation of phenolic hydroxyl by H₂O₂.

The reaction was first conducted with the ns-Fe₃O₄ support, showing that activity of ns-Fe₃O₄ itself is inefficient. The low selectivity of about 60% for 1,4-benzoquinone (BQ) when the reaction temperature is 50 °C indicates overoxidation (Table 1, entry 1). After decreasing the reaction temperature to 25 °C (Table 1, entry 2), the selectivity of BQ decreases to 35.67%, which means ns-Fe₃O₄ itself might not be competent for the oxidation of phenol to BQ in the temperature range commonly used for H₂O₂.

Table 1. Performance of various Fe₃O₄ nanosphere-supported catalysts in phenol oxidation ^a.

Entry	Catalyst	Conv. (%)	Sel. of BQ (%)
1	ns-Fe ₃ O ₄	45.72	60.24
2 ^b	ns-Fe ₃ O ₄	24.73	35.67
3	0.2CuO/ns-Fe ₃ O ₄	92.90	20.71
4 ^b	0.2CuO/ns-Fe ₃ O ₄	79.53	74.62
5	1CuO/ns-Fe ₃ O ₄	94.92	37.75
6 ^b	1CuO/ns-Fe ₃ O ₄	73.71	69.23
7	0.2CoO _x /ns-Fe ₃ O ₄	40.51	27.72

^a Reaction conditions: catalyst 100 mg; H₂O 100 mL; phenol 500 mg; H₂O₂ 6 mL (1 mL/h); temperature, 50 °C; reaction time, 6 h. ^b Temperature, 25 °C.

However, after introducing a small amount of CuO, the sample became highly active, yielding a conversion of 79.53% at a reaction temperature of 25 °C (Table 1, entry 4), which is significantly higher than the 24.73% conversion of ns-Fe₃O₄ alone at the same reaction temperature (Table 1, entry 2). More interestingly, the selectivity for BQ on 0.2CuO/ns-Fe₃O₄ could reach 74.62% under this high conversion rate. An attempt to optimize the temperature to improve the performance of 0.2CuO/ns-Fe₃O₄ was unsuccessful. When the reaction temperature increased to 50 °C, the selectivity for BQ sharply decreased to 20.71% (Table 1, entry 3). This indicates that 0.2CuO/ns-Fe₃O₄ is appropriate for use at 25 °C in the primary oxidation of phenolic hydroxyl and at higher temperatures of about 50 °C for oxidative ring-opening. In addition, by increasing the CuO loading to 1%, both conversion and selectivity were only slightly modified at a reaction temperature of 25 °C (Table 1, entry 6), and the selectivity was still low at a reaction temperature of 50 °C (Table 1, entry 5). Considering its significant potential for improving complexation ability via oxidative ring-opening, 0.2CuO/ns-Fe₃O₄ was chosen as the oxidation modification catalyst for HAs. In addition, support via cobalt oxides, as a common component of Fenton oxidation catalysts [37–41], was also attempted, but the conversion of 0.2CoO_x/ns-Fe₃O₄ (Table 1, entry 7) was much lower than that of 0.2CuO/ns-Fe₃O₄ (Table 1, entry 3).

3.2. Reusability of 0.2CuO/ns-Fe₃O₄

The reusability of the 0.2CuO/ns-Fe₃O₄ catalyst was further tested. The results show that the catalyst was quite stable over five tests, as neither conversion nor selectivity changed significantly (Figure 3). In addition, ICP-OES analysis showed identical Cu loadings before and after five cycles (Table S1, entry 4).

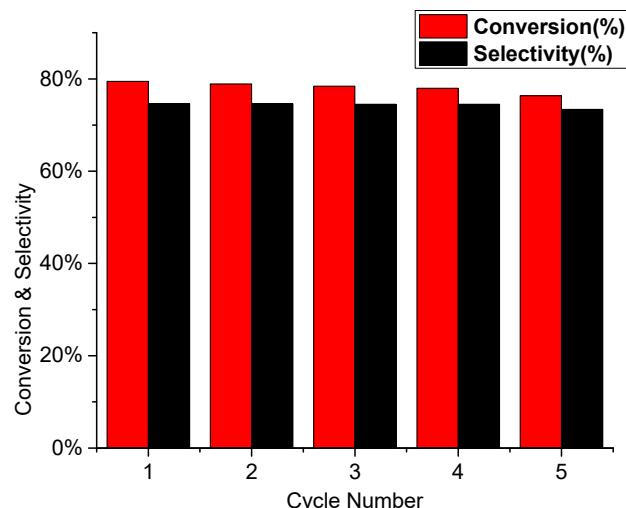


Figure 3. Catalyst recycling experiment for phenol oxidation on 0.2CuO/ns-Fe₃O₄. Reaction conditions: catalyst 100 mg; H₂O 100 mL; phenol 500 mg; temperature, 25 °C; reaction time, 6 h.

3.3. Catalytic Oxidation Modification of HAs

As shown in Table 2, entry 7, carboxylic acid was detected in the humic acid raw material, but its content was relatively low at only 2.45%. The Boehm titration method [42–44] was employed to quantitatively analyze the carboxylic acid content in HAs (details in Section 4). After oxidation at room temperature for 6 h without a catalyst, the carboxylic acid content increased by approximately 1%, reaching 3.26% (Table 2, entry 4), which is still low. After increasing both the reaction time (Table 2, entry 5) and temperature (Table 2, entry 6), the growth rate of acid wt % remained insignificant. However, after adding the 0.2CuO/ns-Fe₃O₄ catalyst, the carboxylic acid content in humic acid increased significantly.

Table 2. Comparison of carboxylic acid contents in humic acid under different reaction conditions.

Entry	Temperature (°C)	Reaction Time (h)	H ₂ O ₂ (mL)	Catalyst Used? Yes (Y)/No (N)	Acid wt (%)
1	50	6	6	Y	10.47
2	70	6	6	Y	10.26
3 ^a	50	12	12	Y	8.24
4	25	6	6	N	3.26
5 ^a	25	12	12	N	4.06
6	50	12	12	N	4.86
7	0	0	0	N	2.45

Reaction conditions: 0.2CuO/ns-Fe₃O₄ catalyst 100 mg; H₂O 100 mL; HAs 500 mg; H₂O₂ 6 mL (1 mL/h). ^a H₂O₂ 12 mL (1 mL/h).

According to the analysis of the reaction results, after oxidation at 50 °C for 6 h under CuO/ns-Fe₃O₄, the acid wt % increased to 10.47% (Table 2, entry 1), which is a fourfold increase compared with the raw material. Through the preliminary exploration, the reaction conditions were optimized. When the temperature was increased to 70 °C, the acid wt % slightly decreased to 10.25% (Table 2, entry 2). Under the conditions of a double oxidant

dosage and an extended reaction time, the acid wt % decreased significantly to 8.24% (Table 2, entry 3). These decreases, as shown in Table 2, entries 2 and 3, might be the result of high temperatures and long reaction times, which caused the carboxyl groups in HAs to be oxidized into other oxygen-containing functional groups. This indicates that the reaction conditions in Table 2, entry 1 are appropriate.

Before and after oxidation, there were minimal changes in the physical properties of the HAs. The HAs modified under the reaction conditions outlined in Table 2, entry 1 were separated and dried (details in Section 4), and a photo was taken for comparison (Figure S5). As observed from Figure S5, the color of the HAs changes from dark black before oxidation to brown after oxidation. Humic acid is composed of the incomplete decomposition products of various types of organic matter, which typically contain large amounts of aromatic and heterocyclic structures. During the oxidation process, these complex organic molecules may be oxidized into smaller molecules, or their conjugated systems may be destroyed, causing changes in the absorbed light wavelength and resulting in the color fading from dark to light. Meanwhile, the oxidation reaction may convert certain functional groups such as alcohols, aldehydes, and phenols into carboxylic acids of higher oxidation states, thereby reducing the molecular weight and altering the solubility and other physicochemical properties. This oxidation effect may lead to the destruction of the original structures and the formation of new structures, thus changing the color of the substance. To confirm this, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were utilized.

Figure 4 shows that before oxidation, HAs appear more uniform and compact. The flake structures overlap with each other and have relatively smooth edges. The particle size is relatively large, and the gaps between particles are small. The surface of HAs after oxidation becomes looser, and large particles disintegrate into smaller particles with more distinct spacing between them. The edges of the particles appear rougher, showing obvious signs of erosion. Based on the FTIR characterization in Figure 5, it is inferred that reactions such as benzene ring C–H bond oxidation, oxidative ring opening, and side chain oxidation occur in HAs. The interlayer forces within the original lamellar structure were weakened, while the generated microbubbles further destroyed the originally compact structure. It is worth mentioning that these structural changes usually help enhance HAs' various properties, such as their adsorption and complexation performance. These changes due to oxidation are commonly reported in HA extraction processes from lignite [45,46].

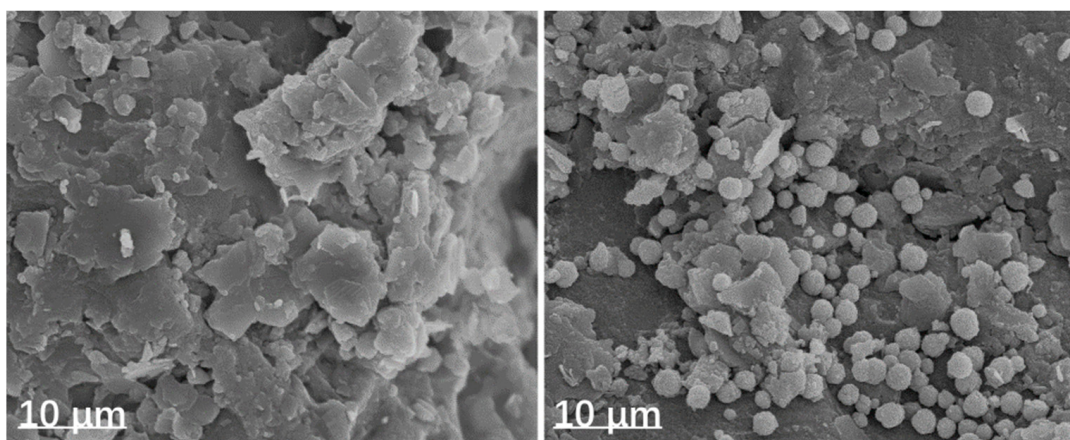


Figure 4. SEM images of HAs before (left) and after (right) oxidation.

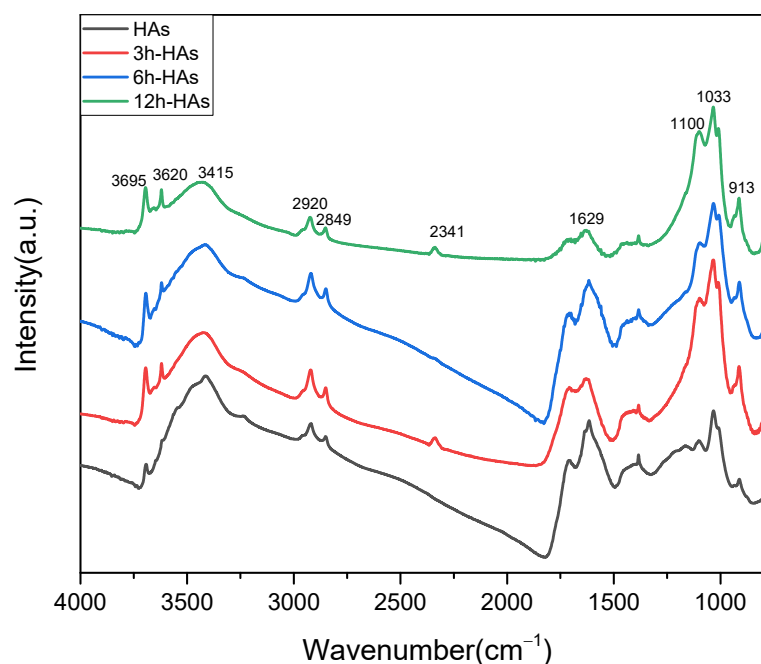


Figure 5. FTIR of HAs at different oxidation times. Reaction conditions: 0.2CuO/ns-Fe₃O₄ catalyst 100 mg; H₂O 100 mL; HAs 500 mg; H₂O₂ 1 mL/h.

The FTIR results (Figure 5) demonstrate significant changes in the functional groups and chemical structure of HAs before and after modification. According to literature reports, sample infrared peaks were assigned [47–50]. After modification, there was increased intensity in the O–H stretching vibration peaks of mineral-associated water at 3415 and 3620 cm^{−1} in the FTIR spectra, indicating that the HAs' original structure was destroyed and that more mineral components were exposed after 3 h of reaction. Meanwhile, the intensity of the hydroxyl group peak at 3415 cm^{−1} decreased, suggesting that oxidation caused hydroxyl groups to be converted into other oxygen-containing functional groups after 12 h of reaction. As shown by the peak at 1629 cm^{−1}, the carbonyl groups in anthraquinone molecules increased with the reaction time but decreased after 12 h, which was possibly due to the oxidation of these molecules in humic acid into diphenol and dicarboxylic acid structures under specific conditions. This is consistent with the increase in the peak of C–H surface deformation and vibration related to unsaturated benzoquinone bonds at 913 cm^{−1}. Interestingly, the C–O stretching peaks of polysaccharide-like substances at 1100 and 1033 cm^{−1} first increase with reaction time up to 6 h and then decrease when the reaction time reaches 12 h. This means that from 6 to 12 h, oxidative modifications developed into over-oxidation, and some oxygen-containing functional groups were converted into CO₂. Additionally, the vibration peaks of aliphatic C–H stretching at 2920 cm^{−1} and 2849 cm^{−1} weakened after 12 h, indicating a decrease in the number of aromatic-ring side chains, which is caused by the oxidation of these chains into phenolic hydroxyl groups.

These changes in functional groups suggest that humic acid underwent structural reorganization during the modification process, leading to the enhanced activity of its functional groups. The changes in anthraquinone molecules and the decrease in carbonyl content together reflect the conversion of unsaturated compounds, while the increase in carboxylic acids indicates the formation of oxygen-containing functional groups. This can enhance its interaction with catalysts, making it an effective catalyst carrier or modifier.

3.4. Investigation of Magnetic Catalyst Separation Performance

Before separating the catalyst from the humic acid using a magnet, first, the modified humic acid needed to be completely dried to remove all moisture. Then, the dried humic

acid was ground and pulverized using physical methods to facilitate the subsequent separation steps. After grinding, a magnet was used for multiple separations through magnetic adsorption effects, taking advantage of the difference between the magnetic catalyst and non-magnetic humic acid, as shown in Figure 6 (for more pictures of separation, see Figure S6). Through repeated application of magnetic separation, the catalyst and humic acid could be effectively separated. Because of the weight gain effect due to the oxidation reaction, the weight of oxidated HAs slightly exceeds that of raw HAs with the weight gain rate reaching 100.22%. Meanwhile, the recovery rate of the catalyst was found to be as high as 99.28%, demonstrating that this method is efficient and reliable for separating magnetic catalysts and humic acid.

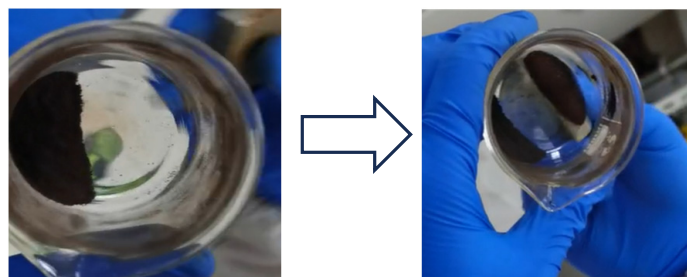


Figure 6. Separation performance of HAs from 0.2CuO/ns-Fe₃O₄ after oxidation, dehydration and grinding.

4. Materials and Methods

4.1. Materials

Ethylene glycol (AR, 98%), ferric chloride hexahydrate (AR, 98.5%), sodium acetate (AR, 98%), cetyltrimethylammonium bromide (98%), hydrogen peroxide solution (30%) and anhydrous ethanol (AR, 99.7%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Anhydrous copper chloride (AR, 98%) and cobalt(II) nitrate hexahydrate (AR, 98%) were purchased from TiTan Technology, Shanghai, China. Deionized water was obtained from a Millipore Autopure system (Merck Millipore, Burlington, MA, USA). Humic acid was purchased from Red Jade Technology, Chengdu, China and extracted from Baoqing lignite in Shuangyashan, China (see a brief description of the extraction steps in the Supplementary Information).

4.2. Characterization

4.2.1. XPS

XPS characterization of the samples was performed using ESCALAB 250XI equipment produced by Thermo Fisher Scientific, Waltham, MA, USA. First, the samples were uniformly spread on double-sided adhesive tape, and a thin layer of powder was produced using clean sampling tools. Then, aluminum foil cleaned with acetone was placed over the samples to prevent contamination. This aluminum foil–sample combination was placed in two-plane stainless steel molds for pressing. After pressing, the aluminum foil covering the samples was removed, and the edges were gently tapped to remove any excess powder on the surface. Then, excess aluminum foil was trimmed from along the edges of the pressed sample to prepare 1 cm × 1 cm specimens, which were then placed on the testing platform for analysis. Monochromatic Al K α radiation (1486.6 eV) was used for testing with a power of 150 watts and a beam spot size of 400 μ m. The C1s peak in the test results was calibrated at 284.8 eV to obtain information about the crystal structure and crystallinity of the samples.

4.2.2. SEM

SEM characterization of the samples was conducted using a Regulus8100 scanning electron microscope manufactured by Hitachi, Tokyo, Japan. First, conductive adhesive was fixed onto the sample stage, and then the powder samples were evenly spread on the surface of this adhesive with any unattached powder gently blown away. Next, the samples were dried under vacuum to prepare for SEM observations. For samples with poor conductivity, gold sputtering treatment was performed to enhance their conductivity, ensuring effective SEM analysis. During the analysis, the testing parameters were adjusted based on the captured images with the working voltage set at 5.00 kV to obtain clear surface images of the samples.

4.2.3. TEM

The TEM, HRTEM, and EDS characterization of magnetic nanoparticle samples was conducted using a Tecnai G2 F20 transmission electron microscope from Thermo Fisher Scientific (FEI), Waltham, MA, USA. First, a small amount of powder sample was placed in a 1.5 mL centrifuge tube, which was followed by the addition of an appropriate amount of absolute ethanol. The mixture was subjected to ultrasonic dispersion for 5 min in an ultrasonic oscillator to ensure uniform sample dispersion. Subsequently, the well-dispersed liquid was drop-casted onto a carbon-coated copper grid and allowed to dry naturally. During TEM analysis, an acceleration voltage of 200 kV was used.

4.2.4. FTIR

FTIR characterization, conducted using a NICOLET IS5 infrared spectrometer from Thermo Fisher Scientific, Waltham, MA, USA, was used to identify the functional groups in HA samples. The spectral resolution was 4 cm^{-1} , the scan number was 40 and the spectral scanning range was $4000\text{--}400\text{ cm}^{-1}$. After mixing the samples with KBr, they were dried under infrared light for approximately 2 h to remove moisture, which might affect the test results. Next, about 1–2 mg of the sample was finely mixed with 200 mg of pure KBr to ensure uniformity. The mixture was then placed in a mold and compressed into a thin pellet using a press machine until it was ready for analysis in the sample cell. The background spectrum was collected in air and automatically subtracted from the tested sample spectrum.

4.2.5. XRD

X-ray diffraction (XRD) patterns were collected using a PW3040/60 X' Pert PRO (PANalytical, Almelo, The Netherlands) diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15432\text{ nm}$), operating at 40 kV and 40 mA. Continuous mode was used for collecting data in the 2θ range from 20° to 90° at a scanning speed of $5^\circ/\text{min}$.

4.2.6. ICP-OES

ICP-OES characterization was conducted using Agilent ICPOES720 produced by Agilent Technologies, Santa Clara, CA, USA. After weighing the sample, approximately 1 mL each of hydrofluoric acid, hydrogen peroxide, and hydrochloric acid was added. After complete dissolution on a 200°C hot plate, the acid volume was adjusted to 3 mL for final volume determination by adding hydrochloric acid; then, the solution was cooled and transferred and instrumental analysis was performed.

4.2.7. VSM

VSM characterization was conducted using a SQUID-VSM produced by Quantum Design, San Diego, CA, USA. An appropriate amount of sample was taken and fixed to the sample rod. First, preliminary measurements of magnetic moment were con-

ducted. Then, an appropriate magnetic field strength and magnetic moment testing range were set. Subsequently, the hysteresis loop of the sample was measured to evaluate its magnetic properties.

4.2.8. Boehm Titration

The Boehm titration method is a chemical analysis technique used to characterize solid acidic or basic functional groups and particularly for studying the surface chemical properties of carbon materials (such as activated carbon, graphene, and carbon nanotubes). This method was proposed by Hans P. Boehm in the 1960s and has been widely applied in materials science and environmental science [51]. Boehm titrations were conducted as reported in [42]. The steps are briefly described as follows:

Sample pretreatment: First, dry the solid sample and sieve it to obtain a certain particle size to ensure the uniformity of the reaction.

Titration reaction: React the solid sample with hydrochloric acid and sodium hydroxide solutions of certain concentrations. Typically, different strengths of acids and bases are chosen to distinguish different types of functional groups.

Filtration and washing: After a certain reaction time, separate the solid sample from the solution by filtration and wash it with deionized water to remove unreacted acids or bases.

Post-processing and analysis: Use appropriate indicators or determine the quantity of remaining acids or bases by titration to calculate the number of different types of functional groups on the sample surface.

4.3. Catalyst Preparation

Fe₃O₄ nanoparticles were prepared via a hydrothermal method. First, 2.7 g of ferric chloride hexahydrate (FeCl₃·6H₂O), 7.2 g of sodium acetate (CH₃COONa) and 4.95 g of cetyltrimethyl ammonium bromide (CH₃(CH₂)₁₅NBr(CH₃)₃) were added to a 0.1 L glycol solution, which was stirred evenly and then reacted in a hydrothermal kettle at 200 °C for 12 h. After the solution had cooled, the product was separated from the solution by magnetic separation and then washed with deionized water and anhydrous ethanol and dried in a vacuum oven at 50 °C for 12 h to prepare uniform Fe₃O₄ nanoparticles.

The 0.2CuO/ns-Fe₃O₄ sample was prepared using a simple impregnation method. A total of 1.2 mg of anhydrous copper chloride (CuCl₂) was dissolved in 0.3 g of water and then mixed with 0.3 g of Fe₃O₄ nanoparticles. After drying at 50 °C for 3 h, it was calcined in a muffle furnace at a temperature of 400 °C for 5 h.

The 1CuO/ns-Fe₃O₄ sample was also prepared using a simple impregnation method. A total of 6 mg of anhydrous copper chloride (CuCl₂) was dissolved in 0.3 g of water and then mixed with 0.3 g of Fe₃O₄ nanoparticles. After drying at 50 °C for 3 h, it was calcined in a muffle furnace at a temperature of 400 °C for 5 h.

The 0.2CoO_x/ns-Fe₃O₄ sample was again prepared using a simple impregnation method. A total of 2.8 mg of Co(NO₃)₂·6H₂O was dissolved in 0.3 g of water and then mixed with 0.3 g of Fe₃O₄ nanoparticles. After drying at 50 °C for 3 h, it was calcined in a muffle furnace at a temperature of 400 °C for 5 h.

4.4. Activity Tests

The phenol oxidation reaction was conducted in a machinery stirring reactor. Typically, 500 mg of phenol was dissolved in 100 mL of ultrapure water in a 250 mL conical flask. Then, 100 mg of CuO/Fe₃O₄ catalyst was added to the conical flask, and stirring was maintained at 50 °C for 6 h. If H₂O₂ was used as an oxidizing agent, it was added at a constant speed. For example, if a 5 mL H₂O₂ solution was added over a 6 h reaction duration, 1 mL of H₂O₂ solution was added at the beginning of the reaction, and then

every 1 h, a further 1 mL of this solution was added to the reaction system until all of it was used up.

Humic acid oxidation was conducted using a similar machinery stirring reactor system. Typically, 500 mg of humic acid was dissolved in 100 mL of ultrapure water in a 250 mL conical flask. Then, 100 mg of CuO/Fe₃O₄ catalyst was added to the conical flask, which was then stirred at 50 °C for 6 h. A total of 5 mL of H₂O₂ solution was added over a 6 h reaction duration; 1 mL of H₂O₂ solution was added at the beginning of the reaction, and then every 1 h, a further 1 mL of this solution was added to the reaction system until all of it was used up.

The catalyst was recycled from humic acid using a magnetic separation method. First, the product was separated by centrifugation at 6000 rad/min for 20 min. Then, the catalyst and product were dried in a 60 °C oven for 6 h. Finally, using a magnet, the catalyst could be separated from the humic acid product. The catalyst was calcined in an air atmosphere for half an hour to remove HAs before weighing.

The product was qualitatively analyzed by gas chromatography–mass spectrometry (GC-MS) on an Agilent 7890B instrument (Agilent Technologies, Santa Clara, CA, USA) equipped with an on-column injector (260 °C), an FID detector (325 °C) and an HP-5 capillary column (30 m × 0.32 mm × 0.25 mm). The conversion and selectivity were calculated by gas chromatography.

The selectivity (denoted as *S* in the formula) of benzoquinone was calculated as follows:

$$S = \frac{N_{\text{BQ}}}{N'_{\text{Ph}} - N_{\text{Ph}}}$$

The conversion (denoted as *C* in the formula) of phenol was calculated as follows:

$$C = \frac{N'_{\text{Ph}} - N_{\text{Ph}}}{N'_{\text{Ph}}}$$

where *N*_{BQ}, *N*_{Ph}, and *N'*_{Ph} represent the mole amounts of benzoquinone after the reaction, phenol after the reaction, and phenol before the reaction, respectively.

5. Conclusions

This paper provides a valuable approach to solving the issues with catalyst separation and recovery encountered in fields such as biomass depolymerization, heavy oil processing, and coal chemistry. By using CuO/ns-Fe₃O₄, an efficient MCS for the oxidative modification of HAs was designed. Under optimized experimental conditions, a significant increase in carboxylic acid content in HAs from 2.45% to 10.47% was achieved, significantly improving their potential industrial value. FTIR and SEM results showed that structural reorganization occurred in HAs during oxidative modification with an increase in free hydroxyl groups and carboxylic acid. These changes promoted the reactivity and coordination complexing ability of HAs. Meanwhile, the recovery rate of CuO/ns-Fe₃O₄ through magnetic adsorption was as high as 99.28%, demonstrating this method's superiority in separating HAs and MCSs. This work provides a reliable methodology for effective and low-cost catalyst separation and recovery by MCSs, which can be used in similar processes, showing sufficient industrial potential.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15121175/s1>, Figure S1: TEM images of Fe₃O₄ microspheres prepared at different cetyltrimethylammonium bromide concentrations; Figure S2: XRD characterization of 0.2CuO/ns-Fe₃O₄; Figure S3: Full XPS spectra of 0.2CuO/ns-Fe₃O₄ (a), and high-resolution XPS spectra of Fe₃O₄, CuO and the Fe-O-Fe elements in Fe₃O₄-CuO (b, c and d); Figure S4: VSM

plots of 0.2CuO/Fe₃O₄ microspheres prepared at different CTAB concentrations; Figure S5: Comparison of HAs that before (left) and after (right) oxidation; Figure S6: Separation pictures of HAs from 0.2CuO/ns-Fe₃O₄ after oxidation, dehydration and grinding; Table S1: ICP-OES results of CuO/ns-Fe₃O₄ and 0.2CoO_x/ns-Fe₃O₄.

Author Contributions: Experiments and Data Analysis: T.L., X.Z. and X.H.; Methodology and Writing: T.L. and G.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, Young Scientists Fund, 22102210.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article and its Supplementary Materials.

Conflicts of Interest: The authors declare no conflicts of interest.

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